9. LUMINESCENCE

And God said, "Let there be light," and there
was light. And God saw that the light was good.
And God separated the light from the darkness.
Bible

9.1. Luminescence mechanisms and their types

The glows of cold bodies (some minerals, fireflies, mushrooms, and rotting wood) have long attracted human attention with their beauty and mystery. The first studies of luminescence date back to the beginning of the XVII century. The phenomenon of luminescence was studied by G. Galileo, R. Boyle, I. Newton and other prominent scientists.

Luminescence is the emission of an excited substance that is excess over thermal and, after the excitation ceases, lasts much longer than the period of light oscillations of the excited atom or molecule (roughly 10^{-14} s for the visible light).

Substances in which luminescence is observed may be in a solid, liquid or gaseous state. Natural and artificial substances that have a bright luminescence are called phosphors. Inorganic crystalline phosphors are called crystalline phosphorus, and amorphous - phosphorus. Organic phosphors are called organoluminophores.

What are the significant differences between thermal and luminescent radiation? Let's call them:

- the duration of the emission of light after the termination of excitation (the so-called afterglow time) considerable exceeds the period of light oscillations);
- luminescence is characterized by a much narrower spectrum of radiation;
- thermal radiation becomes visible at body temperatures above 800 K, while luminescence is a "cold glow";
- increasing the body temperature shifts the maximum of the spectrum of thermal radiation towards shorter wavelengths and at $T > 800$ K the intensity of visible thermal radiation increases;
- in the phosphor, raising the temperature beyond room temperature causes quenching of the luminescence, and cooling – increasing the luminescence.

The centers of luminescence are called elemental emitters, the luminescence of which is the phenomenon of luminescence of crystals and glasses. The basis of the luminescence center can be both a single atom (ion) of the activator of the chemical

element, which is added in the form of an impurity during the cultivation of crystalline phosphorus, and a point structural defect of the lattice, for example, vacancy. The luminescence center combines the activator atom, the surrounding atoms of the lattice and its defects, and atoms of other impurities (co-activators). The activator atom acts as an absorber of excitation energy (directly or through the lattice), which then gives off in the form of light.

Own and impurity luminescence. Intrinsic luminescence is the luminescence of the excitation of a basic substance, such as metal vapor or impurity crystal. In the first case, the atoms themselves radiate, and in the second, the defects of the crystal lattice.

Impurity luminescence is observed in crystals and glasses that incorporate activator atoms or ions (an example is a ZnS crystal: Cu -zinc sulfite activated by copper atoms). Activator atoms (ions) are elemental emitters embedded in the underlying substance.

Depending on the mechanism of illumination of an atom or molecule, there are four mechanisms of luminescence:

- resonant;
- spontaneous;
- forced metastable;
- recombination.

Types of luminescence are distinguished by the method of excitation of a substance that can occur under the action of:

- radiation (photoluminescence);
- electric field (electroluminescence);
- electron bombardment (cathodoluminescence);
- chemical reactions (chemiluminescence and its kind – bioluminescence);
- nuclear particle bombardment (radioluminescence).
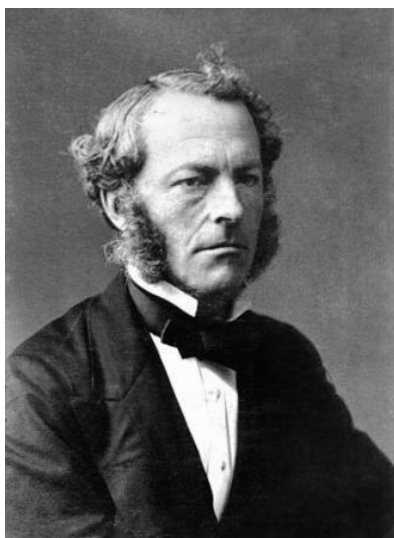
9.2. Photoluminescence

There are two types of photoluminescence – fluorescence and phosphorescence.

A systematic study of photoluminescence was initiated by the English physicist and mathematician George Stokes (Fig. 9.1). In 1852 he formulated a rule for the spectra of excitation and photoluminescent radiation (Stokes rule) [9.1]. Most substances satisfy this rule and they are called Stokes phosphors. However, there are phosphors that violate the Stokes rule and they are called anti-Stokes phosphors.

Photoluminescence is widely used in the mercury fluorescent lamps that we usually see in the classrooms. Such a lamp is filled with argon and contains several milligrams of mercury. An electric discharge ignited in argon vaporizes mercury and excites its glow at wavelengths of 185 and 254 nm. The ultraviolet radiation of mercury causes a white glow of the phosphor deposited on the inner surface of the lamp. The efficiency of fluorescent lamps is several times higher than that of incandescent lamps.

Photoluminescence is also used in food or water quality control. The control method is based on the fact that fresh and stale products, clean and contaminated water differ in luminescence spectra (Fig. 9.2).

Photoluminescence makes it possible to identify a certain type of atoms or molecules in a mixture using the mechanism of resonance luminescence (Fig. 9.3). Atoms and molecules during the process of resonance absorption, i.e. when the energies of the absorbed and emitted photons are equal, both the absorption of light at a certain wavelength and its radiation at the same wavelength sharply increase. Luminescent analysis allows determining the concentration of a specific substance in a mixture up to 10^{-10} g/sm^3.

Stokes rule
The maximum of the photoluminescence spectrum
is shifted relative to the maximum of the absorption spectrum
toward longer waves

Spectrum of anti-Stokes luminescence

Spectrum of excitation
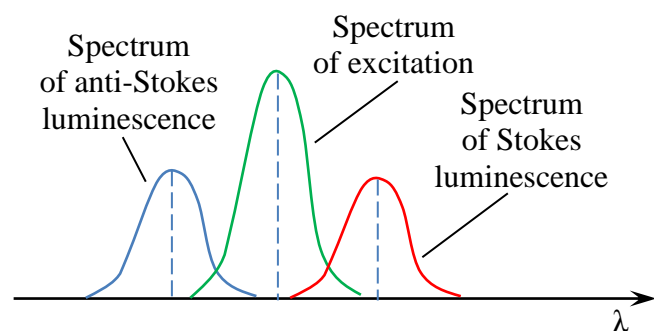
Spectrum of Stokes luminescence

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Fig. 9.1. The English scientist George Stokes (1819–1903) and rule of Stokes shift
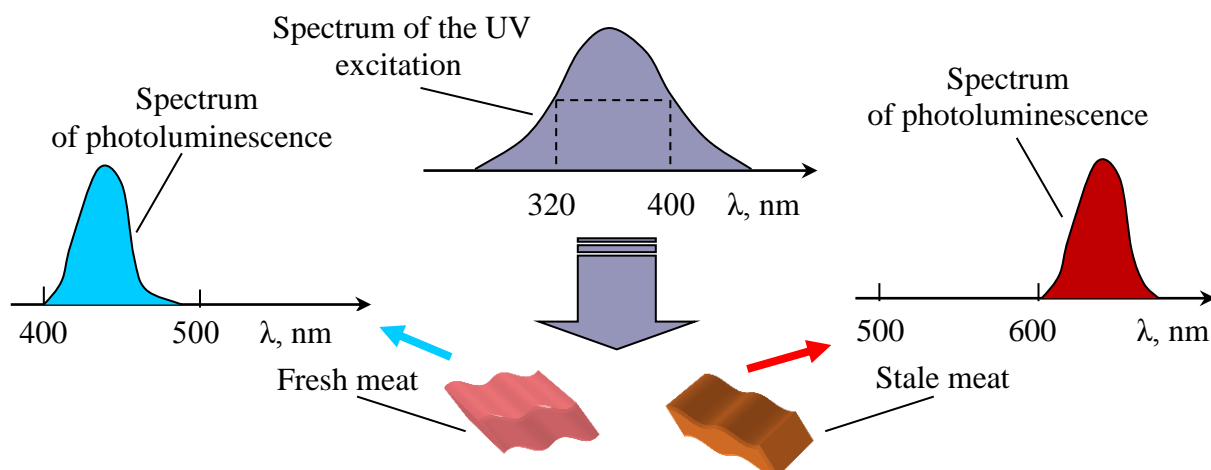
Fig. 9.2. Photoluminescence spectra of fresh and stale meat

This type of luminescence has also found application in microscopy, biology and medicine. In some surgical operations, the patient drinks a glass of orange juice before surgery and the surgeon sees under ultraviolet illumination of the surgical field the glow of the removed tumor. In this case, the property of the tumors to strongly absorb some types of dyes is used (in this case, the natural dye of oranges).

Depending on the afterglow time, luminescence is divided into *fluorescence* (approximately 10^{-8} s) and phosphorescence (significantly longer than 10^{-8} s, sometimes up to several days and even years). Often, fluorescence and
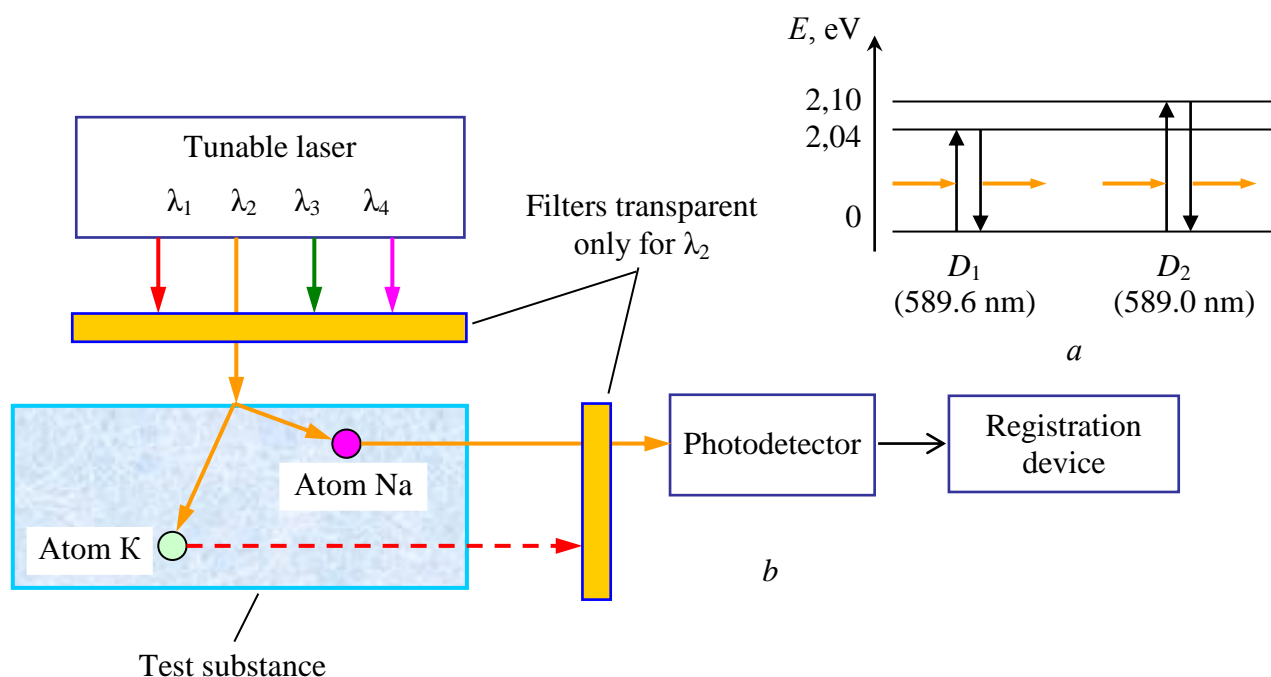

Fig .9.3. Resonance luminescence: laser excitation of a yellow doublet (lines *D*1 and *D*2) of the Na atom (*a*); an illustration of the principle of luminescent analysis (*b*)

phosphorescence are called varieties of photoluminescence. For example, in the «Encyclopedia Britannica» you can read:

«Phosphorescence, emission of light from a substance exposed to radiation and persisting as an afterglow after the exciting radiation has been removed. Unlike fluorescence, in which the absorbed light is spontaneously emitted about 10^{-8} second after excitation, phosphorescence requires additional excitation to produce radiation and may last from about 10^{-3} second to days or years, depending on the circumstances».

Note that a time of 10^{-8} s is a typical lifetime of an atom in an excited state, from which it goes into the ground state with the generation of a photon or the transfer of excitation energy to another particle. Any particle with sufficient energy can cause the excitation of an atom. Fluorescence is observed upon direct transitions of atoms from an excited state to the ground state, occurring without the aid of other particles (Fig. 9.3).

Some atoms have the so-called metastable excited states, from which they cannot pass to the ground states on their own. In order to transfer to the ground state, a metastable atom must receive additional energy from another particle and go from a metastable state to an ordinary excited state with a higher energy. This is the mechanism of action of stimulated (metastable) luminescence (Fig. 9.4).
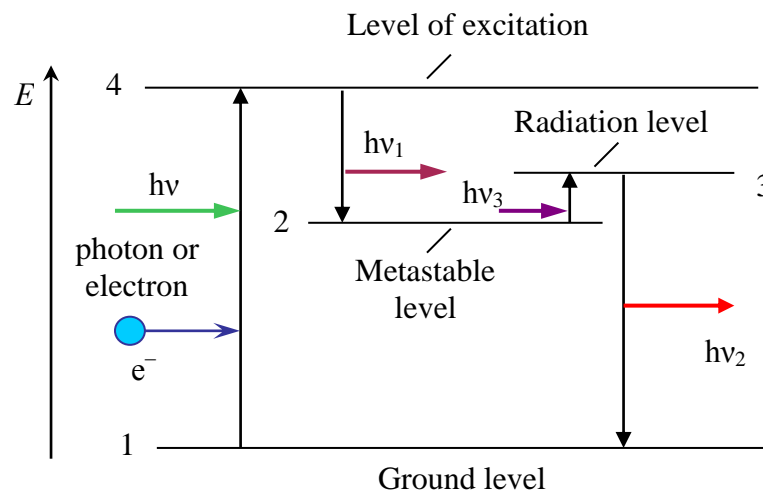

Fig. 9.4. Stimulated metastable luminescence: 1→4 – excitation of an atom by a photon, electron or other particle; 4→2 – transition to metastable level with emission of a long-wave photon or with transfer of energy to a phonon or electron; 2→3 – transfer of energy from phonon, photon or electron to atom; 3→1 – radiative transition

9.2. Cathodoluminescence

On one of the nights of 1675, an incident occurred that entailed many amazing discoveries and eventually led to the development of electronics. The French astronomer Jean Picard, rearranging a mercury barometer, accidentally shook it and saw a glow inside a glass tube. The reason for the appearance of "barometric light" became clear only at the end of the 19th century. A column of mercury descending in a glass tube left electrons behind it on the glass. Electrons detached from the surface of the tube and colliding with molecules of an air caused its glow. In other words, exactly the same electric gas discharge appeared in the barometer as in neon lamps.

In 1706, the English physicist Francis Hauksbee invented an air vacuum pump, which allowed him to obtain a pressure of 10 mm Hg in the pumped-out reservoir. Having partially evacuated air from a glass ball, Hauksbee found that the friction of a rotating ball on his arm causes a glow of air remained in the ball.

In 1855, the German glassblower and physicist Heinrich Geisler invented a mercury vacuum pump that allowed air to be pumped into a glass tube to a pressure of 10^{-3} mm Hg.

The German mathematician and physicist Julius Plucker (Fig. 9.5) was the first in 1858 to observe the phenomenon of glow of a solid in a gas discharge (the phenomenon of *cathodoluminescence* – the glow of matter under the action of an electron beam). This phenomenon helped him to discover the cathode rays in 1859.

Various properties of cathode rays have been studied by English scientist William Crooks. Using a radiometer, he discovered the mechanical action of cathode rays (impeller rotation). Crooks saw that the cathode rays cause phosphorescence of the end of the glass tube they fall on. A metal obstacle creates a shadow on the tube end that can be moved by acting on the cathode rays by a magnetic field.

Studies of cathodoluminescence at the end of the 19th century led to the discovery of an electron (J. Thomson, 1893) and X-rays (W. Roentgen, 1895).

Cathodoluminescence is most widely used in

Fig. 9.5. The German scientist Julius Plucker (1801–1868)

the cathode-ray tubes (CRT) of television sets, computer monitors and oscilloscopes. Cathodoluminescence gives the brightest glow – up to 10^9 candelas/m^2 (about 200 times the brightness of a CRT).

The penetration depth of electrons (in centimeters) into the material can be found from a simple formula [9.2]

$$d = \frac{CW_e^{3/2}}{\rho},$$

where C is the constant, $C = 10^{-5}$ g^2/(cm^2·keV$^{2/3}$); W_e is the electron energy, [keV], and ρ is the material density, [g/cm^3].

For example, electrons accelerated between two electrodes with a potential difference of 10 kV, i.e. having energy of 10 keV, penetrate into the luminophore to a depth of 2.5 microns. More than 90% of the electron energy goes to heating the material, and the rest goes to cathodoluminescence, secondary electron emission and X-ray generation.

Material heating by electron flow is used for electron-beam welding and electron-beam melting. Electronic welding allows combining materials with very different thermo-physical properties, such as aluminum and titanium. Electronic melting is used to obtain very pure metals.

When a metal surface is bombarded with an electron beam with an energy W > 30 keV, X-ray radiation is generated.

9.3. Electroluminescence

Electroluminescence is called optical non-thermal radiation, which lasts for some time after the electric field is switched off. The electric field accelerates the charged particles that exist in a substance, and after disconnecting the field, the particles gradually lose their energy, transferring it to atoms and molecules, ions, electrons, and phonons of the crystal lattice. Excited atoms, molecules and ions, returning to their ground states, emit photons of luminescent radiation. It is obvious that the glow of electric discharge in gases also falls under this definition of electroluminescence.

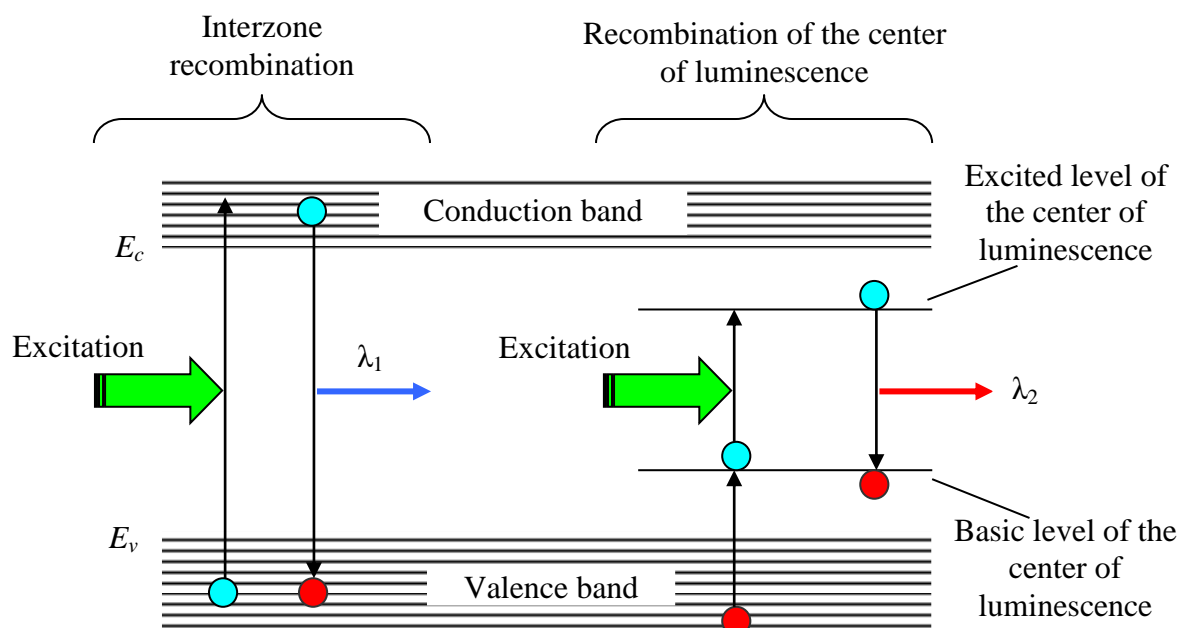There are two important types of electroluminescence in semiconductors, namely:

Fig. 9.6. Recombination luminescence in a semiconductor

- injection electroluminescence upon direct displacement of the *p–n*-junction (applied voltage U > 0) and, as a consequence, injection of electrons into the base and their radiative recombination with holes;

- pre-break electroluminescence upon reverse *p–n*-junction (U < 0) and radiative recombination of electrons and holes, which appeared as a result of an electrical (reversible) breakdown preceding the thermal (irreversible) breakdown.

In semiconductors, recombination luminescence is most often observed (Fig. 9.6). However, spontaneous luminescence is sometimes observed, which is also characteristic of impurity atoms in a solid and complex molecules in vapors or solutions (Fig. 9.7).
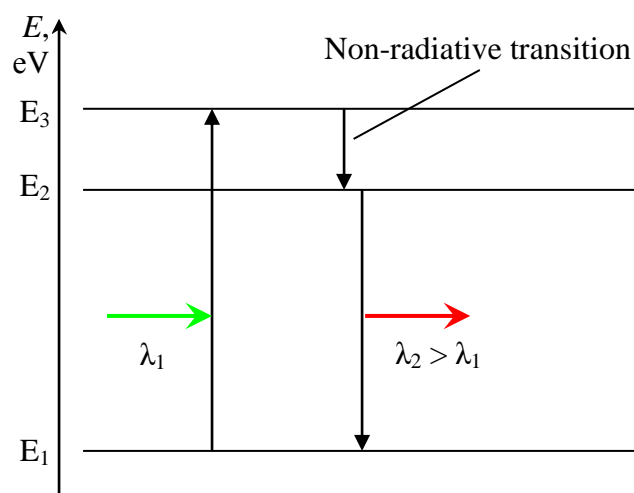

Fig. 9.7. Spontaneous luminescence

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Electroluminescence has found application in the light emitting diodes (LEDs) and laser diodes.

9.4. Chemiluminescence

The fluorescent glow that accompanies exothermic chemical reactions is called *chemiluminescence*. The chemiluminescence intensity is proportional to the rate of chemical reaction and the quantum efficiency of chemiluminescence, which is defined as the ratio of the number of luminescent photons to the number of molecules (reaction products).

As an example, the reaction of hydrogen peroxide with oxalic acid ether, which is accompanied by a rather bright luminescence (quantum efficiency ~ 25 %), can be cited. Similar reactions are used in emergency light sources, which are "switched on" when mixing reagents. Such a source is capable of delivering up to 0.1 lm of light flux per 1 ml of solution.

Bioluminescence is called the chemiluminescent glow of microorganisms, plants, animals, as well as extracts derived from them, which is observed in the visible, rarely – ultraviolet ranges.

9.5. Radioluminescence

The luminescence that occurs when exposed to a phosphor of nuclear particles (α-particles, electrons, protons, neutrons, γ-quanta, etc.), as well as X-rays, is called radioluminescence. These high-energy particles ionize the phosphor atoms and molecules, and the charge carriers accelerate to a speed sufficient for impact ionization, the emergence of an avalanche of secondary electrons, and, as a consequence, a large concentration of excited atoms or molecules. The quantum efficiency of radioluminescence – the number of luminescent photons per particle absorbed – can be much greater than one, although the energy output does not exceed 0.25 (each of the intermediate processes has an efficiency below 100 %).

Radioluminescence is used in detectors of nuclear particles – scintillation counters. Scintillators are inorganic NaJ and ZnS crystals, organic anthracene and stilbene crystals, plastics and liquids with corresponding impurities, as well as inert gases. Absorbing the nuclear particle, the scintillator produces a short-lived ($10^{-5} - 10^{-9}$ s) luminescence flash in the ultraviolet or blue-green regions of the

spectrum. The outbreak is recorded by a photoelectron multiplier directly adjacent to the scintillator.

9.6. References

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